LASER PYROLYSIS-TRANSFER LINE CHROMATOGRAPHY/MASS SPECTROMETRY OF SINGLE, LEVITATED COAL PARTICLES

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INTRODUCTION

A laser pyrolysis transfer line gas chromatograph/mass spectrometry (laser Py-TLGC/MS) system based on the combination of an electronically pulsed CW CO_2 laser with an electrodynamic balance (EDB), a heated capillary ("transfer line") GC column and an ion trap mass spectrometer (ITMS) was constructed (Figure 1), as described previously [1].

The main purpose of the system is to study the devolatilization behavior of single, levitated coal particles at very high heating rates, e.g., 10^5-10^6 K/sec, while comparing the composition of the devolatilization products to those observed at much lower heating rates, e.g., 10^{-2}-10^2 K/sec. At the lower heating rates, several different time-resolved Py-MS techniques, including vacuum thermogravimetry/mass spectrometry (TG/MS) [2], Curie-point Py-MS [3] and pyrolysis Field Ionization mass speetrometry (Py-FIMS) [4] are available to provide kinetic information on coal devolatilization processes. Although kinetic parameters obtained at these lower heating rates may be directly applicable to fixed bed or even fluidized bed coal processes, the usefulness of these parameters for pulverized coal combustion processes at heating rates in the 10^4-10^5 K range remains to be determined. The laser Py-TLG/MS system shown in Figure 1, although not suitable for determining kinetic parameters at these high heating rates, enables us to verify the mechanistic aspects of coal devolatilization reactions. If the main coal devolatilization mechanisms remain unchanged at 10^5-10^6 K/sec, it may be argued that it should be possible to extrapolate the kinetic parameters obtained by the abovementioned TG/MS, CuPy-MS and Py-FIMS experiments.

CO_2 laser devolatilization experiments on single levitated coal particles using EDB type particle trapping devices have previously been described by several authors [5-7]. However, although successful in measuring particle temperatures and/or weight loss profiles as a function of time none of these prior studies addressed the characterization and identification of the complex mixture of devolatilization products generated during these experiments. To the best of our knowledge, the work reported here represents the first successful attempt to do so.

EXPERIMENTAL

The experimental set-up (Figure 1) consists of an EDB, a 50 w CW CO_2 laser and a Finnigan MAT ITMS system. The particle levitation cell was constructed in such a way as to provide line-of-sight access to the center of the cell for the CO_2 laser beam as well as for visual observation by means of a stereo microscope and for a two-color optical pyrometer (under development). Typical cell operating parameters for levitating a 120 µm dia. Spherocarb particle are: ring electrode 3000 V (60 Hz ac), upper end cap +100 V dc, lower end-cap -100 V dc.

The CO_2 laser (Apollo 3050 OEM) is capable of electronic pulsed beam operation. The 8 mm dia. beam is split equally into 2 opposing beams focussed at the center of the levitation cell (beam waist ca. 400 μm, power density ca. 4-10 MW/m^2). A co-linear parfocal HeNe laser beam permits positioning the levitated particle in the optical and electrical center of the cell. Two IR detectors measure the integrated pulse and time-resolved pulse energy.

A heated transfer line column (2m x .18 mm DB5) equipped with a special air sampling inlet [8] enables intermittent sampling of volatiles from the center of the levitation eell into the ITMS vacuum system.

Feasibility studies were performed on 120-150 μm Spherocarb particles impregnated with ng amounts of an alkylnaphthalenes mixture and other selected model compounds. Finally, a series of experiments was performed with actual coal particles in the 100-130 μm size range, prepared by careful sieving of coals from the Argonne National Laboratory Premium Coal Sample (ANL-PCSP) program.

RESULTS AND DISCUSSION

Before applying the laser Py-TLGC/MS technique to coals, we measured the shot-to-shot reproducibility of the electronically pulsed CW CO_2 laser system. As illustrated in Figure 2 overall linearity of the laser pulse energy in the 1-35 msec range is quite good. However, the cause of the unexpectedly large variation in pulse energy at 20 msec is being investigated further.

System performance was further tested with 120-130 μm sized Spherocarb particles loaded with known quantities of a well characterized mixture of alkylnaphthalenes and related aromatic compounds. Figure 3 shows the time-resolved TLGC/MS profiles obtained by using the 6 ft long heated transfer line between EDB and ITMS as a short capillary column. Various alkylnaphthalene homologs and isomers are readily separated and identified. Moreover, repeated laser pulse heating of the same Spherocarb particle shows that the devolatilization process is virtually complete within the duration of the first pulse (10 msec).

This encouraged us to perform laser Py-TLGC/MS analyses on real coal particles. The resulting TLGC/MS profiles shown in Figures 4 and 5 demonstrate a surprising level of chemical detail. Repeat analyses of Pittsburgh #8 coal shown in Figure 4 demonstrate an acceptable level of shot-to-shot reproducibility in spite of the unavoidably high heterogeneity of 100-150 μm dia. coal particles, Figure 4c illustrates the fact that, at these high heating rates oxygen does not markedly influence the devolatilization process. Apparently, the rapidly expanding and cooling cloud of devolatilization products surrounding the particle effectively protects the hot particle surface from severe oxidative changes.

As mentioned earlier, the main goal of the EDB-ITMS experiment is to verify the effect of high heating rates on devolatilization mechanisms. Assuming that any significant shift in mechanisms should be reflected in changes in the relative abundances of various structural isomers, e.g., alkylsubstituted phenols or naphthalenes, Figure 5 enables a side by side comparison of laser Py-MS profiles and more conventional Curie-point Py-GC/MS profiles obtained on samples of Pittsburgh #8 coal. Obviously, little if any changes in product distributions are observed, when allowing for interparticle heterogeneity as well as for differences in chromatographic techniques. A high degree of correspondence between coal devolatilization products observed at 10^2 K/sec and at 10^5 K/sec was also found to exist for other ANL-PCSP coals (not shown here).

However, due to the inherently low tar yields of both the Beulah Zap lignite (see Figure 6) and the low volatile bituminous Pocahontas coal satisfactory laser pyrolysis mass spectra of single, levitated particles of these coals proved difficult to obtain. Therefore, it is too early to conclude that no significant mechanistic changes are observed at these high heating rates. Moreover, careful examination of the laser pyrolysis TLGC/MS profiles revealed the absence (or strongly reduced intensity) of dihydroxybenzenes and of long chain (e.g., C_{10}-C_{20}) n-alkane/alkene pairs. Whether these compounds are lost by secondary condensation reactions in the hot outer layers of the particle or by some other chemical or physical process is currently the focus of further investigations.

As noted earlier, a marked degree of interparticle heterogeneity is expected to exist in pulverized coals. Provided that a high level of shot-to-shot reproducibility can be achieved, the laser Py-TLGC/MS approach could become a powerful tool for studying interparticle heterogeneity. A preliminary indication of the effects of interparticle heterogeneity on successive laser Py-TLGC/MS profiles can be obtained from the bivariate plot in Figure 7. The clustering trends observed in the intensities of the peaks at m/z 94+108 and m/z 142+156 appear to be relatively independent of pulse length (except for very short laser pulse deviations which result in incomplete devolatilization reactions). At this point, differences in maceral and mineral composition between different particles are thought to be primarily responsible for the clustering behavior observed in Figure 7.

CONCLUSIONS

In conclusion, laser Py-TLGC/MS appears capable of producing a detailed chemical profile of the devolatilization products from single, levitated coal particles at very high heating rates (~10^5 K/sec), especially when using coals which produce relatively high tar yields. Most devolatilization products detected at these high heating rates appear to be identical to those observed at much lower heating rates, e.g., 10^{-2}-10^2 K/sec, indicating that coal devolatilization mechanisms remain essentially unchanged over some 7 orders of magnitude difference in heating rates!

A few compound classes found to be missing or strongly reduced, e.g., dihydroxybenzenes and long chain aliphatic hydrocarbons, are though to be lost by secondary condensation reactions. Another interesting observation is the absence of marked oxidative phenomena when performing laser pyrolysis TLGC/MS experiments in air rather than under inert atmospheric conditions. Apparently, the rapidly expanding and cooling vapor cloud protects the hot surface of the particle. Finally, it is concluded that interparticle heterogeneity has a marked effect on laser Py-TLGC/MS profiles and that this technique therefore offers a unique opportunity to study the effect of interparticle heterogeneity on coal devolatilization processes.

ACKNOWLEDGEMENTS

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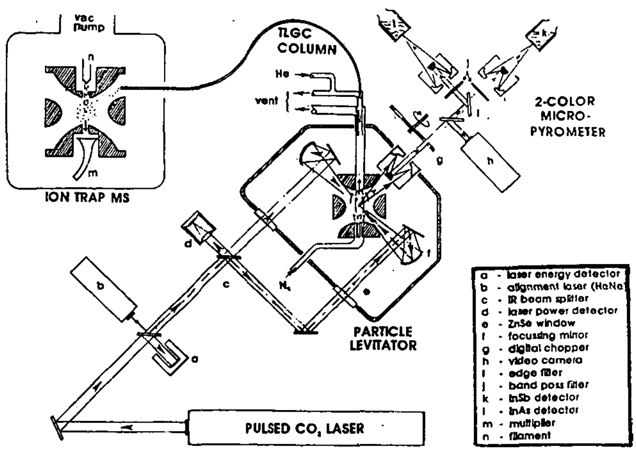

Figure 1. Schematic diagram of CO_2 laser pyrolysis TLGC/MS system consisting of a pulsed CO_2 laser, an electrodynamic balance ("particle levitator), a transfer line GC column and an ion trap mass spectrometer. The 2 color micropyrometer is currently under development.

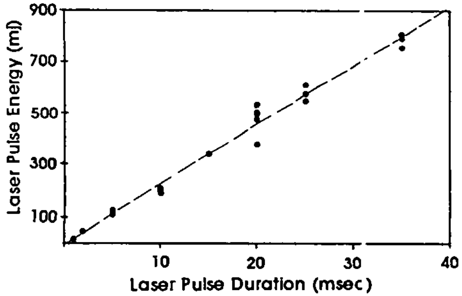

Figure 2. Variability in laser pulse energy at different pulse lengths.

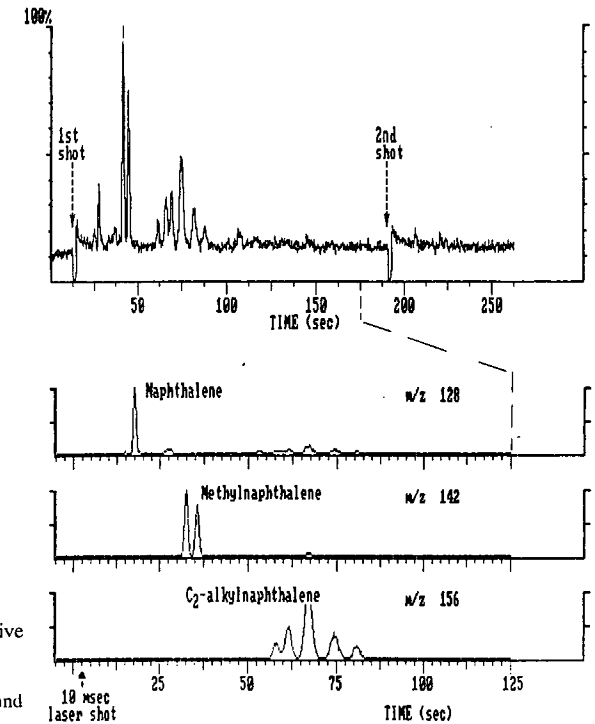

Figure 3. Total ion chromatogram (top) shows 2 consecutive laser shots at same Spherocarb particle (impregnated with alkylnaphthalenes mixture). Selected ion chromatograms illustrate TLGC separation of alkylnaphthalene homologs and isomers. Column temp: 50-200 C in 2 minutes.

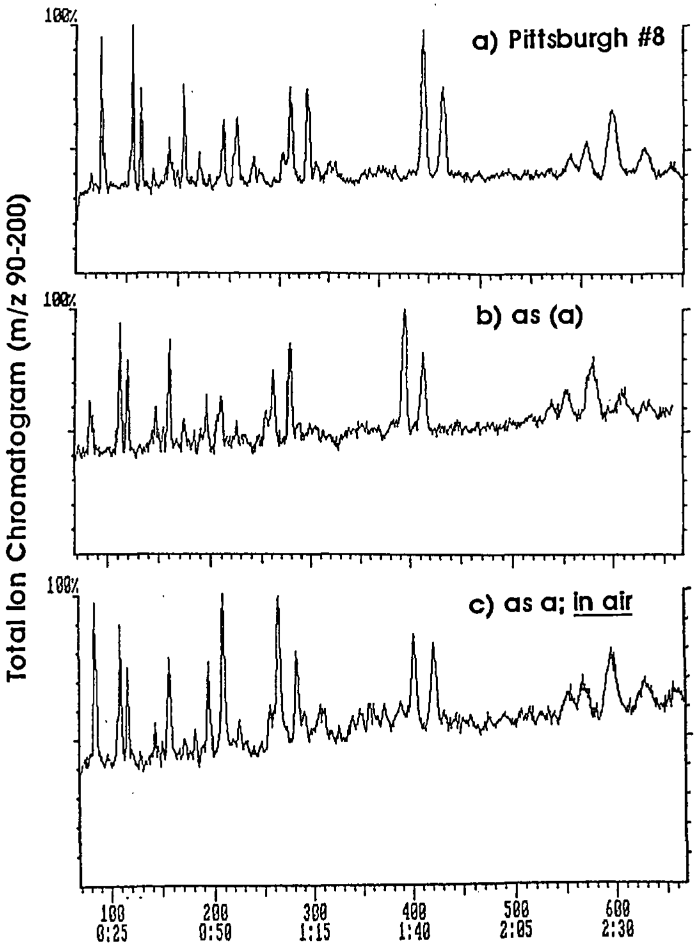

Figure 4. Repeatability of Laser Py-TLGC/MS profiles of single Pittsburgh #8 coal particles. Profile (c) falls within normal range of variation!

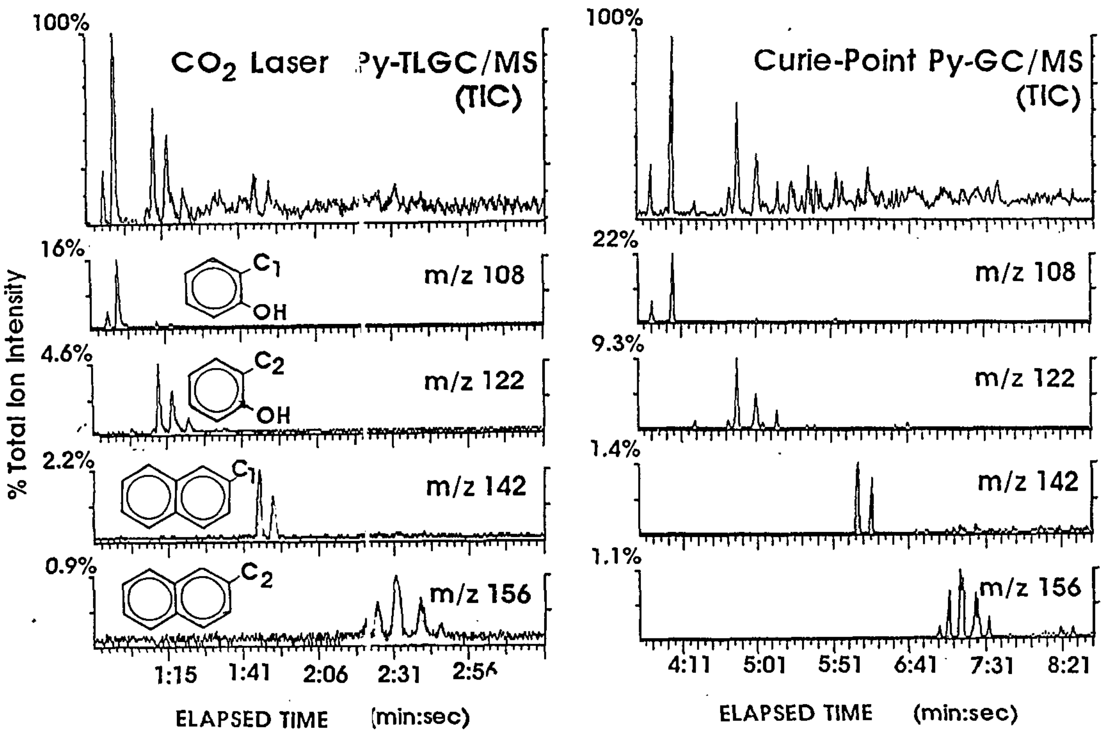

Figure 5. Comparison of CO_2 Laser Py-TLGC/MS profiles obtained at high heating rates (~10^5 K/sec) with Curie-point Py-GC/MS profiles obtained at lower heating rate (~10^3 K/sec). Note similar relative abundances of major tar components.

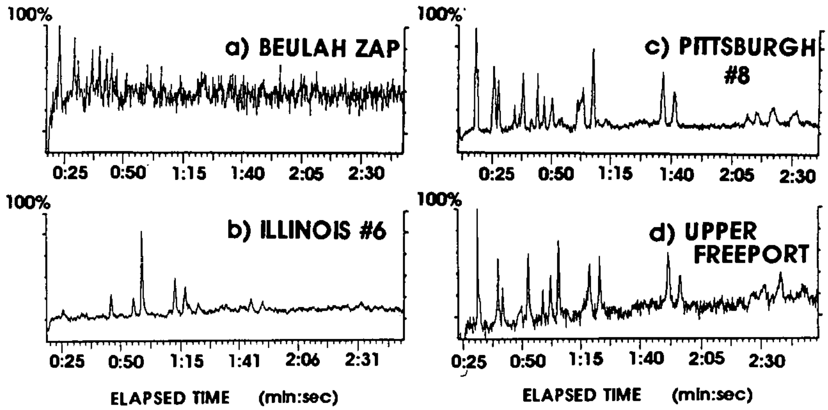

Figure 6. Comparison of laser Py-TLGC/MS profiles of 4 ANL-PCSP coals of different rank. Note lower signal-to noise ratio for Beulah Zap lignite and Upper Freeport, mvb coal compared to hvCb Illinois #6 and hvAb Pittsburgh #8 coals.

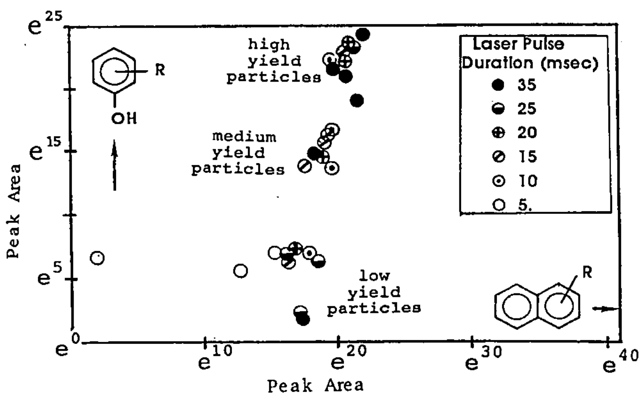

Figure 7. Scatter plot of peak areas at m/z 142 + m/z 156 (x-axis) vs. m/z 94 + m/ 108 (y-axis) from TLGC/MS profiles of 26 Illinois #6 coal particles analyzed at 6 different pulse lengths. Note variable naphthalene response at 5 msec (due to incomplete devolatilization) and presence of 3 phenol yield levels independent of pulse length (thought to be due to differences in maceral content).